

First Octahedral Platinum Cluster: Structure as a Function of Electron Count in Pt₆ Clusters

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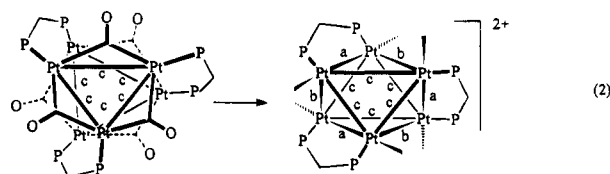
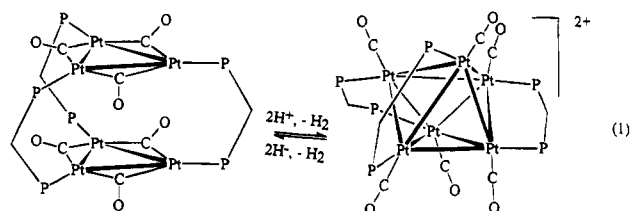
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Although many platinum cluster complexes have been isolated, hexanuclear clusters have remained elusive, and there are no reported octahedral Pt₆ clusters.¹ The only simple Pt₆ cluster remains the anionic [Pt₆(μ-CO)₆(CO)₆]²⁻,² which has distorted trigonal prismatic stereochemistry, although several clusters are now known in which two [Pt₃(μ-CO)₃(PR₃)₃] or related clusters sandwich a main group metal atom.³ This article reports two new types of Pt₆ clusters, which are interconvertible by the gain or loss of two electrons and one of which is shown to have octahedral stereochemistry.

Reduction of equimolar amounts of [PtCl₂(SMe₂)₂] and [PtCl₂(dppm)], dppm = Ph₂PCH₂PPh₂, with NaBH₄ under a CO atmosphere gave the dark red-purple, air-sensitive cluster [Pt₆(μ-CO)₆(μ-dppm)₃], **1**, in high yield.⁴ Cluster **1** is characterized spectroscopically to have a structure in which two Pt₃(μ-CO)₃ triangles are bridged by three μ-dppm ligands; it has approximate D_{3h} symmetry; **1** is isostructural with the palladium analog which was reported recently and whose structure was determined crystallographically,⁵ and its spectroscopic properties are very similar to those of trinuclear clusters [Pt₃(μ-CO)₃(PR₃)₃].³ In particular, the IR and NMR data establish that all carbonyl and CH₂ groups and phosphorus atoms are equivalent and that the carbonyls are doubly bridging. There is no evidence for intertriangle metal–metal bonding, and it can be considered

as two clusters of the known type [Pt₃(μ-CO)₃L₃]^{1,3} held together only by the μ-dppm ligands.

Complex **1** is easily oxidized to give the brown-black cluster cation [Pt₆(CO)₆(μ-dppm)₃]²⁺, **2** (eqs 1 and 2).⁶ In **2**, the IR



and NMR data clearly show that the carbonyl ligands are terminal. In the room temperature NMR, the carbonyl and CH₂ groups and phosphorus atoms are equivalent, but each resonance splits into two equal intensity resonances at low temperature.⁶ This cluster was characterized crystallographically as the BPh₄⁻ salt, and the structure is shown in Figure 1.⁷

The metal core in **2** is roughly octahedral, but there are distortions from regular geometry. In particular, there are three sets of Pt–Pt distances. Those bridged by the dppm ligands (a, eq 2) are shortest, those perpendicular to the C₃ axis (c, eq 2) are intermediate, and the remaining bonds (b, eq 2) are longest. The structural changes on conversion of **1** to **2** are illustrated in eqs 1 and 2. The Pt₃ triangles are twisted to go from the trigonal prism to the octahedron, with the carbonyl and phosphine ligands moving out of the Pt₃ plane, and the carbonyl groups moving from bridging to terminal positions. Complex **2**, in idealized form, thus has D₃ symmetry, consistent with the room temperature NMR data, although the low-temperature NMR data indicate a lower symmetry C₃ ground state geometry. The C₃ axis is retained on moving from **1** to **2** as is clear in eq 2.

The three known Pt₆ clusters have different electron counts and geometries. Clusters **2**, **1**, and [Pt₆(μ-CO)₆(CO)₆]²⁻, **3**, have 82, 84, and 86-electron configurations and have octahedral, 2 × triangular, and trigonal prismatic geometries, respectively. It is interesting that either oxidation or reduction of the 84-electron clusters leads to a net attraction between the triangular units.^{1,2} PSEPT theory predicts that an octahedral cluster should require an 86-electron configuration, but the lower number for **2** is not surprising since platinum typically uses only two p-orbitals in bonding.^{1,2} The cluster [Rh₆(μ₃-CO)₄(CO)₆(μ-dppm)₃] is structurally related to **2** but has an additional four μ₃-CO groups and has the 86-electron configuration, while [Pd₆(μ₃-CO)₄(PMe₃)₇] has a very different ligand environment compared to **2** but has an octahedral metal core and an 82-electron configuration.⁸ To gain further insight into the bonding in **2**, EHMO calculations were carried out on the model complex [Pt₆(CO)₁₂]²⁺, **4**, in which the dppm ligands of **2** are replaced

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(2) (a) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225. (b) Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968. Note that [Pt(μ-Cl)₂]₆ has an octahedral core of platinum atoms but there is no Pt–Pt bonding. Brodersen, V. K.; Thiele, G.; Schneringer, H. G. *Z. Anorg. Allg. Chem.* **1965**, *337*, 120.

(3) (a) Imhof, D.; Venanzi, L. M. *Chem. Soc. Rev.* **1994**, 185. (b) Tanase, T.; Horiuchi, T.; Yamamoto, Y.; Kobayashi, K. *J. Organomet. Chem.* **1992**, *440*, 1. (c) Hallam, M. F.; Mingos, D. M. P.; Adatia, T.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1988**, 335. (d) Albinati, A.; Dahmen, K.-H.; Demartin, F.; Forward, J. M.; Longley, C. J.; Mingos, D. M. P.; Venanzi, L. M. *Inorg. Chem.* **1992**, *31*, 2223. (e) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1994**, *217*, 121.

(4) Yield of **1**: 96%. Anal. Calcd for C₈₁H₆₆O₆P₆Pt₆: C, 39.0; H, 2.7. Found: C, 39.4; H, 2.8. IR (Nujol): ν(CO) = 1790 (vs), 1773 (s, sh) cm⁻¹. NMR in CD₂Cl₂ at 22 °C: δ(¹H) = 4.29 [s, 6H, ³J(PtH) = 44 Hz, CH₂ of dppm]; δ(¹³C) = 240.5 [1:8:18:8:1 quin, 6C, ¹J(PtC) = 757 Hz, μ-CO]; δ(³¹P) = 37.6 [s, 6P, ¹J(PtP) = 5289, ²J(PtP) = 274 Hz, ³J(PP) = 236 Hz]. NMR in CD₂Cl₂ at -90 °C: δ(¹H) = 4.51 [s, br, 6H, CH₂ of dppm]; δ(³¹P) = 36.7 [s, 6P, ¹J(PtP) = 5289 Hz, ²J(PtP) = 277 Hz, ³J(PP) = 216 Hz]. Note that the equimolar mixture of [PtCl₂(dppm)] and [PtCl₂(SMe₂)₂] is conveniently prepared *in situ* by addition of dppm (1 mol) to [PtCl₂(SMe₂)₂] (2 mol) in THF.

(5) Holah, D. G.; Hughes, A. N.; Krysa, E.; Magnuson, V. R. *Organometallics* **1993**, *12*, 4721.

(6) Typically, **1** was oxidized by reaction with CF₃CO₂H to give 2(O₂-CCF₃)₂ in 98% yield (the byproduct is presumed to be H₂). IR (Nujol): ν(CO) = 2015 (vs) cm⁻¹. NMR in CD₂Cl₂ at 22 °C: δ(¹H) = 5.27 [s, 6H, ³J(PtH) = 62 Hz, CH₂ of dppm]; δ(¹³C) = 174.6 [s, 6C, ¹J(PtC) = 1284 Hz, CO]; δ(³¹P) = 11.0 [s, 6P, ¹J(PtP) = 3633 Hz, μ-dppm]. NMR in CD₂Cl₂ at -90 °C: δ(¹H) = 6.08 [s, br, 3H, CH₂H of dppm], 4.76 [s, br, 3H, CHH^β of dppm]; δ(¹³C) = 179.6 [s, 3C, ¹J(PtC) = 1290 Hz, CO]; 171.4 [s, 3C, ¹J(PtC) = 1300 Hz, CO]; δ(³¹P) = 14.0 [s, 3P, ¹J(PtP) = 3810 Hz, μ-dppm], 8.4 [s, 3P, ¹J(PtP) = 3423 Hz, μ-dppm]. Coalesced at -50 °C, δ(¹H) = 5.45 [s, br, 6H, CH₂ of dppm]; δ(¹³C) = 173 [v br, CO]; δ(³¹P) = 11.0 [s, br, 6P, ¹J(PtP) = 3700 Hz, μ-dppm]. **2** has also been prepared as salts with PF₆⁻ or BPh₄⁻ by anion exchange, with BF₄⁻ by reaction of **1** with Cu(NCMe)₄BF₄ or with ReO₄⁻ by oxidation of **1** with Re₂O₇. **2** can be reduced to **1** by reaction with NaBH₄/CO.

(7) X-ray data for 2[BPh₄]₂·CH₂Cl₂·0.5(C₂H₅)₂O·H₂O: C₁₃₂H₁₁₅B₂Cl₂O₇P₆Pt₆; fw = 3270.1; triclinic, space group P1; a = 18.676(4) Å, b = 19.556(5) Å, c = 21.149(5) Å, α = 108.27(1)°, β = 105.52(1)°, γ = 109.83(1)°, V = 6266(4) Å³, Z = 2, R₁(F) = 0.0737, wR₂(F²) = 0.2049 for 5540 observations with F > 4σ(F) with maximum 2θ = 40°.

(8) (a) Ceriotti, A.; Ciani, G.; Garlaschelli, L.; Sartorelli, U.; Sironi, A. *J. Organomet. Chem.* **1982**, *229*, C9. (b) Klein, H. F.; Mager, M.; Florke, U.; Haupt, H. *Organometallics* **1993**, *12*, 4721. (c) The 84e cluster [Pt₆(SO₂)₃(CNXy)₃] is thought to have capped trigonal bipyramidal geometry. Haggitt, J. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1994**, 1013.

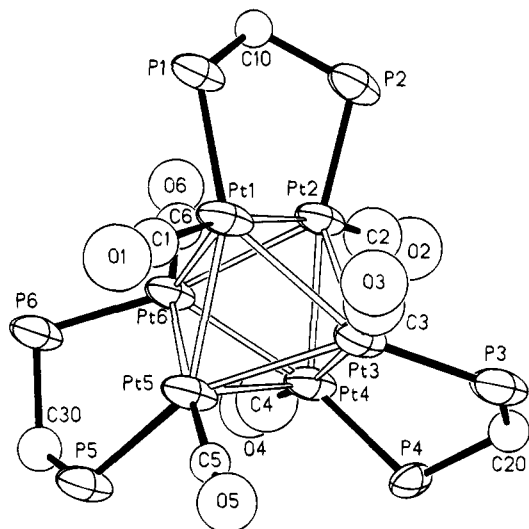


Figure 1. View of the structure of the cation $[\text{Pt}_6(\text{CO})_6(\mu\text{-dppm})_3]^{2+}$ (phenyl groups omitted). Metal-metal distances (\AA) followed by bond type: Pt(1)-Pt(2) = 2.649(3), a; Pt(1)-Pt(3) = 2.808(3), c; Pt(1)-Pt(5) = 2.799(2), c; Pt(1)-Pt(6) = 2.907(2), b; Pt(2)-Pt(3) = 2.916(2), b; Pt(2)-Pt(4) = 2.781(2), c; Pt(2)-Pt(6) = 2.802(2), c; Pt(3)-Pt(4) = 2.665(2), a; Pt(3)-Pt(5) = 2.784(2), c; Pt(4)-Pt(5) = 2.883(3), b; Pt(4)-Pt(6) = 2.790(3), c; Pt(5)-Pt(6) = 2.656(2), a.

by CO. The frontier orbitals of a $[\text{Pt}(\text{CO})_2]$ fragment are hybrid $d_{xz}p_x$ (occupied, A) and sp_z (vacant, B) orbitals. In the D_3 conformation the overlap of these orbitals within each original Pt_3 triangle is weak and the MOs originating from the fragment orbitals A and B are easily identified (Figure 2). This is clearly an unfavorable conformation for the C_3 $[\text{Pt}_3(\text{CO})_6]^+$ unit. However, there is now strong bonding between the two triangular units as shown in Figure 2. Three strongly bonding MOs ($1e + 2a_1$) are formed by overlap of the e combination of fragment orbitals A and the a_1 combination of fragment orbitals B, and all are occupied. The orbital $2a_1$ is the HOMO. The a combination of fragment MOs A overlap only weakly and give MOs $1a_1$ and $1a_2$ (Figure 2). The simplest application of the PSEPT theory would predict that six fragment MOs A would give three bonding and three antibonding MOs while the six fragment MOs B would give one bonding and five nonbonding or antibonding MOs and that the four bonding MOs would be occupied; this would lead to an 80-electron count. The EHMO calculations confirm the presence of four bonding MOs but indicate that the weakly antibonding MO $1a_2$ is occupied (Figure 2), thus leading to an 82-electron count. The calculations also predict the relative strengths of the nonequivalent Pt-Pt bonds as shown by the correlation of overlap populations in 4 and

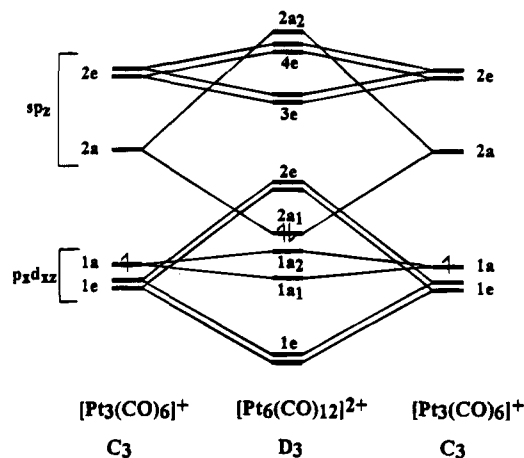


Figure 2. Correlation diagram for formation of $[\text{Pt}_6(\text{CO})_{12}]^{2+}$, with D_3 symmetry, from two $[\text{Pt}_3(\text{CO})_6]^{2+}$ fragments, with C_3 symmetry.

Table 1. Correlation of Overlap Populations for the D_3 Structure of $[\text{Pt}_6(\text{CO})_{12}]^{2+}$ with the Observed Mean Pt-Pt Distances in 2

Pt-Pt bond ^a	OP(Pt-Pt) ^b	mean $d(\text{Pt-Pt})/\text{\AA}$
a	0.22	2.66
b	0.15	2.90
c	0.18	2.79

^a See eq 2 for definitions. ^b OP = overlap population.

average Pt-Pt distances in 2 given in Table 1 and thus indicate that the variations are due to asymmetry in cluster bonding and not to the presence of $\mu\text{-dppm}$ ligands in 2. The 82-electron count is clearly required in order to fill the radial, strongly Pt-Pt bonding MO, while leaving the strongly antibonding orbitals vacant. This is therefore likely to be the favored electron count for octahedral platinum clusters. Clusters 1 and 2 appear to be the first examples of platinum clusters differing only by two electrons and so are important in establishing the dependence of structure on electron count in clusters where only partial use of tangential orbitals is invoked.¹

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Supporting Information Available: Details of the X-ray structure determination and tables of X-ray data (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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